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(Commemoration Issue Dedicated to
Professor Sango Kunichika On the Occasion
of his Retirement)

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The Reaction of Nitrosobenzene with Benzylamine in Non-Aqueous Media

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The reaction of nitrosobenzene with benzylamine was investigated. Nitrosobenzene radical anion, phenylhydroxylamino radical, phenylnitroxide, and benzylphenylnitroxide were observed in the course of the reaction by the analyses of esr spectra. Formation of amino radical was confirmed by the product analysis. It was suggested that the nitrosobenzene radical anion, phenylhydroxylamino radical, and phenylnitroxide were intermediates in the *out of cage* reaction yielding azoxybenzene. Benzylphenylnitroxide and amino radical were also supposed to be intermediates in the *in cage* reaction yielding benzylidenedianiline and ammonia.

INTRODUCTION

It has been well known that nitrosobenzene is of a strong electron accepting nature and produces a variety of paramagnetic species in the reaction with electron donors.¹⁾ In the non-aqueous reaction of nitrosobenzene with amines at low temperature vigorous evolution of ammonia gas was recognized and several kinds of paramagnetic species were observed in the course of the reaction by esr technique. These facts prompted us to investigate the reaction. Suzuki and Weisburger²⁾ have already investigated the reaction at a fairly high temperature (80~82°C). They have described the formation of carbonyl compounds, azoxybenzene, and ammonia to suggest a tentative reaction mechanism. However, the formation of the paramagnetic species could not be independent of the main course of the reaction. The reaction, therefore, was reinvestigated by the analysis of paramagnetic species as well as the product analysis.

EXPERIMENTAL

Materials. Nitrosobenzene was recrystallized from dry ethanol several times in the dark and dried in vacuum, which was stored in the dark under nitrogen atmosphere at 0°C. The sample thus prepared contained no paramagnetic impurities. Benzylamine and *n*-hexane were dried over sodium metal and distilled into a reaction vessel under vacuum before use.

Measurement of Esr Spectra. Known amounts of nitrosobenzene, benzylamine, and *n*-hexane were sealed into respective compartments with the breakable seals (Fig. 1). The seals were broken just before the esr measurement at a desired temperature.

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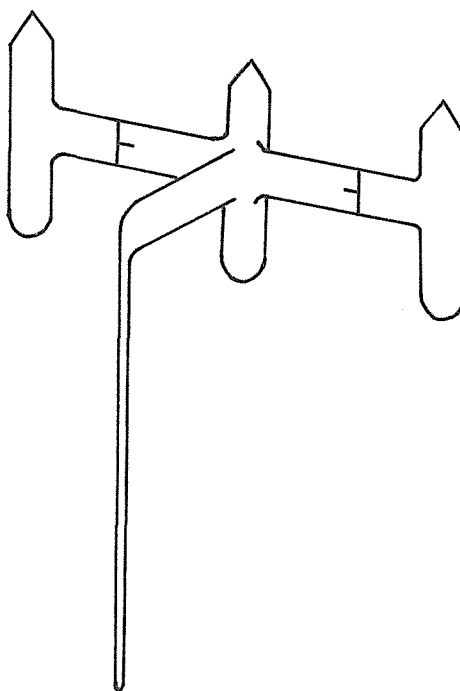


Fig. 1. Sample cell for esr measurement.

During the measurement the sample in esr cavity was maintained at a desired temperature by flow of nitrogen evaporated from liquid nitrogen. A Type JES-ME-3X spectrometer with 100 kHz field modulation from Japan Electron Optics Laboratory Co. Ltd. was used in this experiment. Hyperfine coupling constants, g -values, and total width of the spectra observed were calibrated by using peroxyamine disulfonate. Frequency was measured within an accuracy of 0.03%.

Typical Procedure of the Reaction. Known amounts of nitrosobenzene (2 mM), benzylamine (5 mM), and n -hexane (10 mM) were mixed under vacuum in the dark in a sealed vessel equipped with manometer. The reaction temperature was controlled by circulating water at 25°C. After 24 hrs, gaseous products were submitted to analyses by infrared and mass spectroscopy. Solid products were separated by thin layer chromatography. The separated products were submitted to the analysis for identification.

Identification of Products. Reaction products identified in this reaction by several methods are tabulated in Table I. All observed infrared spectra coincided well with the Sadtler Standard Spectra. Melting points observed were consistent with literature values. Results of elemental analysis and nuclear magnetic resonance of several products are given below. *Azoxybenzene*, mp 35–36°C Found: C, 72.54; H, 5.27; N, 13.90%. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.09; N, 14.13%. τ 1.5–2.7 (6H, aromatic protons). *Azobenzene*, mp 67–68°C. Found: C, 78.40; H, 5.69; N, 15.33%. Calcd for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.38%. τ 2.0–2.7 (6H, aromatic protons). *Benzylidenedianiline*, Found: C, 86.34; H, 6.00; N, 7.69%. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73%. τ 1.6 (1H, CH proton) τ 2.0–2.9 (6H, aromatic protons).

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Table 1. Products in the Reaction of Nitrosobenzene with Benzylamine.

Products		Identified by	Amount of products.
Ammonia	NH_3	ir, ^{a)} mass.	Large ^{e)}
Azoxybenzene	$\phi\text{N}=\text{N}\phi$ O	ir, nmr, ea, mp.	Large
Azobenzene	$\phi\text{N}=\text{N}\phi$	ir, nmr, ea, mp.	Small
Benzylideneaniline	$\phi\text{CH}=\text{N}\phi$	ir, nmr, ea.	Small
Water	H_2O	mass.	Very small
Hydrazine	$(\text{H}_2\text{N})_2$	spot test. ^{b)}	Trace
phenylhydroxylamine	ϕNHOH	tlc. ^{c)}	Very small
Benzaldehyde	ϕCHO	tlc. ^{d)}	Very small

mass: mass spectroscopy, ea: elemental analysis, ir: infrared spectroscopy,
mp: melting point, TLC: thin layer chromatography

- a) Measured with 10 cm gas cell at vapour pressure of 40.0 torr.
- b) See ref. 7.
- c) Developed with standard reagent by use of solvent mixture chloroform-acetone (5 : 1) or chloroform-ethanol (9 : 1).
- d) 2,4-dinitrophenylhydrazine obtained was developed using chloroform as developing solvent.
- e) One mole was produced in the reaction of 2M of nitrosobenzene with larger amount than 1M of benzylamine.

RESULTS AND DISCUSSIONS

Nitrosobenzene is known as a strong electron acceptor.¹⁾ The infrared spectrum of the compound shows intense absorption at 1407 and 1391 cm^{-1} (Fig. 2). Since absorption coefficients of nitroso group is large, we assigned these bands to nitroso group. Aliphatic nitroso compounds have in general an absorption band at about 1600 cm^{-1} region. The extraordinary red shift suggests that the force constant of the NO bond in the nitroso group is weakened by conjugation with phenyl group, and the bond order is less than 2, indicating the overlap of π -orbital of nitroso group with that of phenyl group.

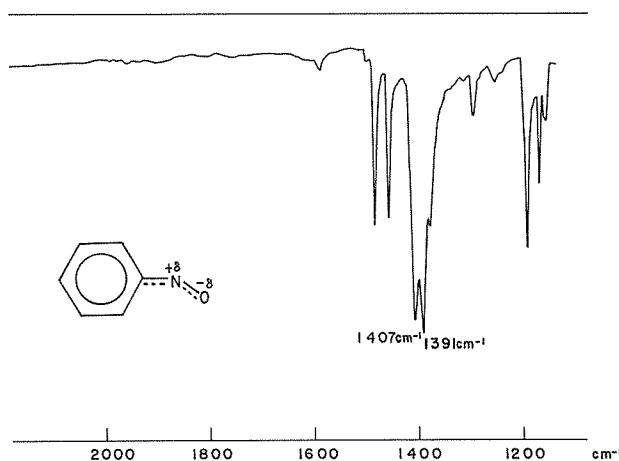


Fig. 2. Infrared spectrum of nitrosobenzene by KBr disc method.

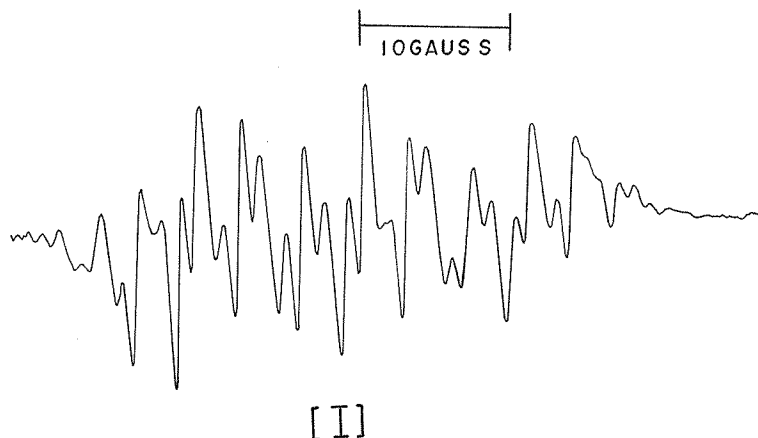


Fig. 3. Esr spectrum of reaction intermediate assigned to nitrosobenzene radical anion [I].

Thus, the lowest unoccupied π -orbital may accept electron from the other compounds easily.³⁾ Dipole moment of nitrosobenzene is also fairly large, *i.e.* 3.17 D at 25°C.⁴⁾ This large value may be one of the factors of high electron affinity.

Immediately after mixing of nitrosobenzene and benzylamine at 0°C the esr signal as shown in Fig. 3 can be observed. This signal may be assigned to nitrosobenzene radical anion [I]* by comparing the signal with that of the reported.^{1,5,6)} Nitrosobenzene radical anion survives for a while, but the spectrum is modified within about ten minutes by appearance of other paramagnetic species.

After thirty minutes from initiations of the reaction at 0°C, esr spectrum changes to that as shown in Fig. 4. The spectrum is assumed to be due to phenylhydroxylamino radical [II-a] which is a tautomer of phenylnitroxide [II-b] or due to the time-averaging of the two [II]. This assumption can be rationalized by comparing the synthetic esr spectrum with the observed. The semi-empirically constructed spectrum based on the following assumption, $a^N=12.4$, $a_{OH^H}=6.4$, $a_{o,o,p^H}=3.2$, and $a_{m,m^H}=1.1$ gauss, coincided well with that of the observed (total width: 43.0 gauss, $g = 2.0059$) as shown in Fig. 4. Russell and co-workers have reported the coupling constants of phenylnitroxide [II-b] as $a^N=9.10$, $a_{NH^H}=11.90$, $a_{o,o,p^H}=3.0$, and $a_{m,m^H}=1.14$ gauss.

Comparing the reported coupling constants for phenylnitroxide [II-b] with ours the values of coupling constant of hydrogen atoms on phenyl group coincide with each other, but the found coupling constant of hydrogen atom of hydroxyl group seems to be large for phenylhydroxylamino radical [II-a]. These facts may be explained by assuming the rapid time average between phenylhydroxylamino radical [II-a] and phenylnitroxide [II-b]. Ayscough and co-workers⁶⁾ suggested that their spectrum was a time averaged one resulted from a rapid tautomerization between phenylnitroxide and its tautomer. But, this was revised and the spectrum was reassigned to $\phi-\overset{\text{O}}{\underset{\text{O}}{\text{N}}}-\text{OH}$.¹⁾ The spectrum is quite different from the observed spectrum in this work.

* Intermediates indicated by Roman numeral were detected by esr method. The spectra are given in Figs. 3, 4 and 5.

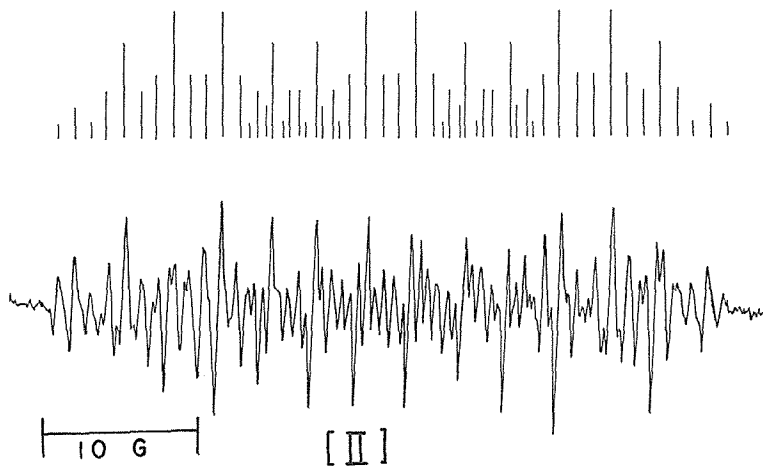


Fig. 4. Comparison of the esr spectrum assigned to the time average of two species phenylhydroxylamino radical [II-a] and phenylnitroxide [II-b] with synthetic spectrum based on the following hyperfine coupling constants: $a^N=12.4$, $a_{OH}^H=6.4$, $a_{o,o,p}^H=3.2$ and $a_{m,m}^H=1.1$ gauss.

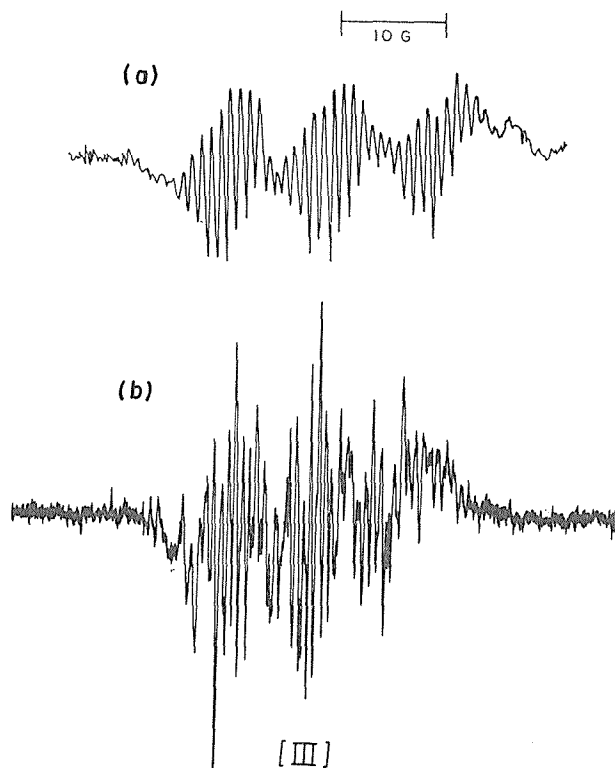


Fig. 5. Esr spectrum assigned to N,N-benzylphenylnitroxide [III].

- a) Width of field modulation: 0.1 gauss.
- b) Width of field modulation: 0.02 gauss.

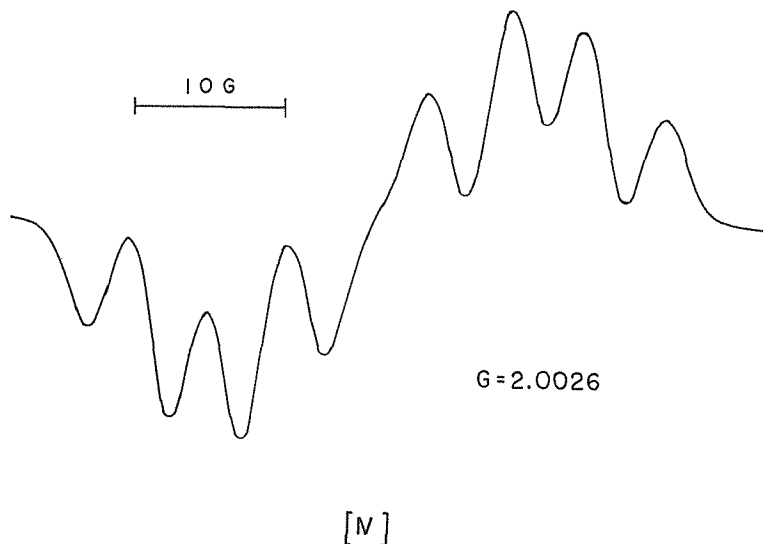
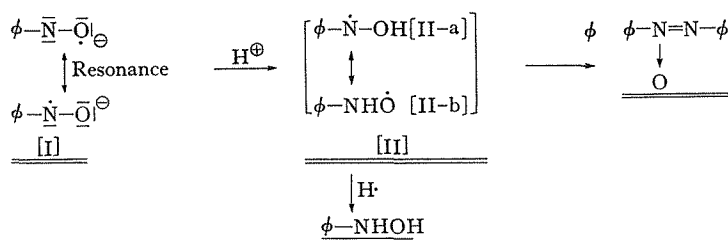
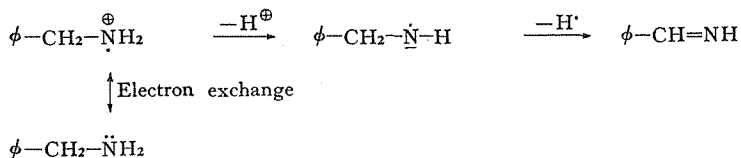


Fig. 6. Esr signal appeared at the last stage of reaction.

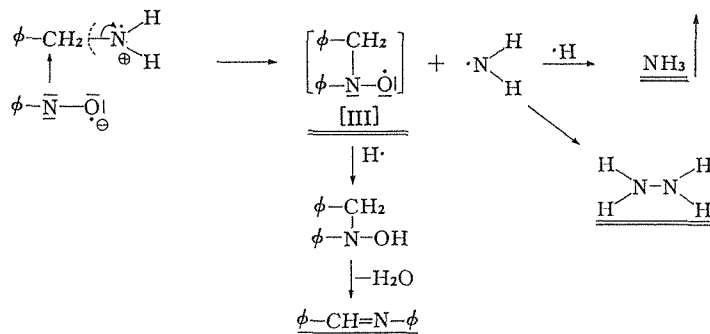
After about forty minutes from initiation of the reaction ammonia gas started to evolve vigorously and continued for about five hours (at 0°C). After two hours esr spectrum varied as shown in Fig. 5. The nature of this spectrum is not clear yet, but an attention is to drawn to the formation of benzylideneaniline as a reaction product, which suggests a transient appearance of *N,N*-benzylphenylhydroxylamine. Thus, the spectrum might be ascribed to benzylphenylnitroxide [III]. Subsequently, esr signal due to the paramagnetic species remained in the reacting mixture changed to that as shown in Fig. 6. The broad signal remained to survive for three days at room temperature.

Results of elemental analyses and nmr of reaction products are given in the experimental section. The formation of hydrazine and of a large amount of ammonia suggests the appearance of amino radical. Summarizing the results described above and taking into consideration of the reaction products identified, the following reaction mechanism is proposed tentatively.

[Out of cage]



[In cage]



Doubly underlined are reaction intermediates and products identified. Nitrosobenzene radical anion [I] will change gradually to phenylhydroxylamino radical [II-a] or its tautomer, *i.e.* phenylnitroxide [II-b], and to azoxybenzene finally through the same path as suggested by Russell⁸⁾ and by Oae.⁹⁾ On the contrary to the experimental result, the esr signal due to benzylamine radical cation should be observed on the course of the reaction in accordance with the reaction scheme described above.

This may be ascribed to the line broadening due to the rapid electron exchange between benzylamine radical cation and benzylamine neutral molecule which is abundant in the reaction system and so the esr line may be too broadened to be observed.

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